

*XXIV. On the Production of nitrous Acid and nitrous Air. By
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1. IT has been known for some time, that a relation subsists between nitrous acid and volatile alkali. The latter has frequently been produced by help of the former; but I do not recollect that, in any instance, the volatile alkali has been proved to contribute to the formation of nitrous acid or nitrous air. Some cases, however, have occurred to me where this evidently happens; and they appear so new and extraordinary, that I cannot but think they deserve the attention of philosophical chemists. The history of the experiments I allude to is as follows.

2. As soon as I had heard of the production of inflammable air by the transmission of steam through red-hot iron tubes, I had the curiosity to try whether some other substances in the form of air or vapour might not, by a similar process, undergo material alterations. In particular, the nitrous acid seemed well to deserve a trial, both on account of the obscurity and difficulties attending the theory of its production, and also of its important and extensive usefulness in chemistry.

In the relation of my experiments on this head, it will be unnecessary to mention the exact quantity of acid or of air expended or generated, though I noted those quantities pretty accurately

accurately at the time; for the main point I have in view in this description, is to ascertain the *nature* of the *changes* which took place; and these do not depend upon the quantities of aerial fluids, but upon their properties. Besides, whoever shall repeat these experiments will find the relative *quantities* to vary very much, according to the manner of operating; and therefore, for the sake of brevity, I omit to mention them entirely.

3. I began with boiling a little strong nitrous acid in a small retort, the neck of which was closely luted to one end of a gun-barrel. The other end of it was immersed sometimes in water, and sometimes in quicksilver, and eighteen or twenty inches of the middle part was surrounded with burning charcoal in a proper furnace. In this manner the vapour and fumes of the boiling acid were transmitted through the red-hot tube, and the produce received at the end in the usual manner.

When the acid was made to boil violently, there passed over a considerable quantity of undecomposed red nitrous vapour, together with a mixture of nitrous and phlogisticated airs.

When the process was conducted more moderately, there was less nitrous vapour; and in the mixture of airs which was received in the glass vessels, there was a much greater proportion of phlogisticated air.

4. In order to increase the surface of the red-hot iron, and effect a more complete decomposition of the nitrous vapour, the gun-barrel was crammed full of iron filings. The experiments were repeated with great caution, and almost the whole of the produce was found to be phlogisticated air. It is however proper to mention, that, notwithstanding every possible care, still there will generally be in some degree an admixture

of nitrous air, and frequently of dephlogisticated nitrous air. But I am satisfied that if the iron tube were sufficiently long, so that a very large portion of it might be heated red-hot, all the air received in this manner from any quantity of nitrous acid slowly boiled would be found of that species called phlogisticated air.

5. These experiments seem altogether analogous to those of Dr. PRIESTLEY, in which nitrous air, by exposure to iron, is converted first into dephlogisticated nitrous air, and afterwards into phlogisticated air. The only difference seems to be, that in my experiments the effect is brought about suddenly; whereas in the method of exposition to iron much time is required. And farther, in my method of operating, it is very difficult to conduct the process so as to insure the production of that singular species of air called dephlogisticated nitrous air. If the acid boil very quick, the product is nearly all nitrous vapour and nitrous air. If it boil very slow, and a sufficient quantity of the iron tube be well heated, then the decomposition is almost complete, and little is received but phlogisticated air. In both cases, the progress of the conversion of nitrous acid to the state of phlogisticated air seems to be the same. First, nitrous air is formed, then dephlogisticated nitrous air, and lastly phlogisticated air. This, I say, seems to me to be the natural order of the conversion, though I do not deny, that in the rapid manner of operating with the red-hot iron tube some particles of nitrous acid or vapour may probably be *instantly* changed into phlogisticated air. And even allowing this to be the case, the fact may easily be explained, by supposing the successive approaches to phlogisticated air to be made in too small spaces of time to be observed; nor does it in the least invalidate the general conclusion, that nitrous air

air is nearer the state of phlogisticated air than nitrous acid or nitrous vapour; and that dephlogisticated nitrous air is still nearer. It is very difficult to decide with certainty what the changes are which the particles of the acid undergo in their passage through different parts of the hot tube.

From what has been said, the most common process will probably appear to be, that a particle of the acid in the form of vapour first generates nitrous air; that the parts of this are applied to fresh surfaces of hot iron, and suddenly changed into dephlogisticated nitrous air; which, lastly, is applied to still fresh surfaces of the tube or fragments of iron, and so converted into phlogisticated air. When these successive contacts with fresh surfaces of hot iron are not sufficiently numerous or exact, it is not unnatural to conclude, that some portion of air may escape not perfectly decomposed.

6. These considerations induced me to alter the process a little. Instead of boiling the acid in the retort, I put some thin pieces of copper into a phial, poured nitrous acid upon them, and forced the nitrous air, as it was generated, to pass through the red-hot tube. The event answered my expectation; the decomposition was effected in this way easier than in the former.

But before I made this experiment, I examined what would be the effect of mere heat upon nitrous air, as I had already learned from the experiments of others, that nitrous acid, forced in the form of steam through red-hot tubes of clay or glass, underwent the most important alterations.

What might be the effect of long continued exposure to a red heat I cannot say; but I was soon convinced, that nitrous air might be forced through a red-hot glass tube, without suffering any material change.

7. Lastly, I determined to try the effect of the gun-barrel upon dephlogisticated nitrous air, as from all that I had seen it seemed reasonable to expect, that this species of air would be the easiest reduced to the state of phlogisticated air. For this purpose, I diluted a saturated solution of copper in the nitrous acid, and put pieces of iron wire into it, and as the neck of the retort which contained the solution was luted to one end of the gun-barrel, the dephlogisticated nitrous air was exposed in its passage to the action of the red-hot tube, and also to the surfaces of the red-hot iron turnings which it contained. In this case, when the process is conducted with proper care, all the air which is received at the other end of the tube will be found phlogisticated.

8. When the air received at the end of the gun-barrel was in the last mentioned state, *viz.* perfectly phlogisticated, I have frequently observed a white fume issuing along with the air, and sometimes ascending through the water or mercury into the glass receivers. Upon examining this white fume, I soon perceived by the smell that it contained volatile alkali. I was much struck with the observation, and immediately recollecting Dr. PRIESTLEY's relation of a similar production by exposing nitrous air to pieces of iron.

9. Most of the experiments hitherto related were made in the summer of 1786; in general they agree with those of Dr. PRIESTLEY; the changes and productions are much the same, and the only new circumstance is, as was observed at art. 5. The same effects are brought about *instantly* by the action of red-hot iron, which require much time by the method of simple exposure to cold iron.

For which reason, though it gave me much pleasure at the time to see such curious transmutations brought about in a few minutes,

minutes, yet it scarcely appeared worth while to trouble the Royal Society with a detail of the experiments; and I only presume to do it now, because the conjectures which I then formed have been sufficiently verified by future experiments.

The conjectures were as follow:

10. Almost immediately upon seeing the volatile alkali produced by means of nitrous acid and metals, I conceived the possibility of inverting the order of the process, and of producing nitrous acid or nitrous air by the decomposition of volatile alkali. I knew of no experiments wherein this had been done, or any thing like it; yet as volatile alkali was beyond all dispute produced in the method just described, and as the iron turnings and inside of the gun-barrel were left after the operation in a state of calcination, it seemed not unnatural to suppose, that by forcing volatile alkali through the red-hot calces of some of the metals, nitrous acid or nitrous air might be produced. Some of my friends, to whom I mentioned the idea, considered it as a random conjecture. However, I made a memorandum of it as a thing that deserved to be tried, though in fact I neglected for near two years actually to make the trial. It was some time in the month of March, 1788, that the calx of manganese on account of its very great infusibility, and its yielding abundance of dephlogisticated air, occurred to me as a very proper substance for the purpose. I immediately crammed a gun-barrel full of powdered manganese; and to one end of the tube I applied a small retort, containing the caustic volatile alkali. As soon as the manganese was heated red-hot, a lighted candle was placed under the retort, and the vapour of the boiling volatile alkali forced through the gun-barrel. Symptoms of nitrous fumes and of nitrous air soon discovered themselves,

and

and by a little perseverance I was enabled to collect considerable quantities of air, which on trial proved highly nitrous. I have since frequently repeated this experiment, and have always in some degree succeeded. Much depends on the *kind* of manganese employed, much on the heat of the furnace, and much on the patience of the operator; as these are varied, there will be great variations of the products. A minute detail of all the particulars of my experiments seems unnecessary; but it may be proper to give a general account of the principal facts, and of the methods which were used to avoid erroneous conclusions.

11. In general I made use of clean gun-barrels with which no previous experiments had been made. The manganese was used in rough powder; for when it is too finely powdered, the tube is choaked, and the air cannot pass.

In some experiments I applied the vapour of the volatile alkali directly to the hot manganese. In others I suffered the manganese to remain a considerable time in a red heat before I made the volatile alkali, contained in the retort at the end of the tube, to boil; and by this means I informed myself of the nature of the airs which the manganese yielded *per se*.

In neither case could I ever perceive the least appearance of nitrous acid or nitrous air till the volatile alkali was used. Manganese, *per se*, gives airs of different kinds (but chiefly fixed and dephlogisticated airs) as soon as ever it is subjected to a considerable heat; but nothing nitrous comes from it, either on the first application of heat, or after it has been continued a long time; and I examined this point with great diligence. But soon after the volatile alkali begins to be applied, the jars in which the air is received will frequently turn slightly

slightly red, and this redness will increase on admitting atmospherical air.

The caustic alkali should be strong, and as far as I have observed the longer the process is continued, the stronger will be the nitrous air produced. At least this evidently appeared to be the case in several instances, where the operation was continued for a long time.

In most instances, on the very commencement of this process, a small jar of the air thus collected discovers by the *smell* a nitrous impregnation. But it sometimes happens, that several jars of air may be collected, and the admission of atmospherical air to them will not produce a sensibly red colour.

Here, however, there exists a cause of deception against which the operator ought to be on his guard, lest he should conclude that no nitrous air is formed, when in reality there is a considerable quantity. The volatile alkali, notwithstanding every precaution, will frequently pass over in great quantities undecomposed. If the receivers are filled with water, a great part of this will indeed be presently absorbed; but still some portions of it will mix with the nitrous air formed by the process. Upon admitting the atmospherical air, the nitrous air is decomposed, and the red nitrous fumes instantly combine with the volatile alkali. The receivers are presently filled with white clouds of nitrous ammoniac; and in this manner a wrong conclusion may easily be drawn, from the want of the orange colour of the nitrous fumes. A considerable quantity of nitrous air may have been formed, and yet no orange colour appear, owing to this circumstance; and therefore it is easy to understand how a small quantity of nitrous air may be most effectually disguised by the same cause.

12. These observations are made principally for the sake of those who may wish to repeat these experiments. The main point to be established, is the actual formation of nitrous air by this method. And this truth I consider as proved beyond all controversy ; for by continuing the process patiently, and applying repeatedly fresh portions of strong volatile alkali to the same manganese, kept constantly hot in the gun-barrel, I have often collected large jars of air, which was proved to be highly nitrous by mixture with atmospherical or with dephlogisticated air.

13. It is not easy to say, whether in this process dephlogisticated nitrous air, or even nitrous acid itself, be not sometimes immediately formed by the action of the volatile alkali on the manganese. Traces of the former, in some instances, seem to discover themselves ; but I do not speak decidedly on this head. As to the latter, it is very certain, that fumes of the nitrous acid often circulate in the jars that receive the air. But possibly these fumes may arise from the decomposition of nitrous air, by means of the superfluous dephlogisticated air of the manganese.

14. The steam of boiling water was applied to red hot manganese in a similar way ; not the least nitrous appearance ; but the fixed and dephlogisticated airs were generated much more plentifully than when the manganese was urged by mere heat. When these airs had been collected in large quantities, the volatile alkali was applied as before to the residuum of the manganese, and nitrous air soon appeared.

15. As manganese is known to produce a very extraordinary change upon spirit of salt in a moderate heat, it seemed not improbable, that a still greater change might take place by working in this method. Accordingly I forced the vapour of

boiling spirit of salt to pass through red-hot manganese. This experiment did not answer my expectation ; the product was a mixture of fixed and inflammable air. But it deserves to be noticed, that even in this case, after the effect of the spirit of salt had been tried for a long time, a production of nitrous air upon the application of volatile alkali to the same manganese soon took place.

16. As there are many other substances besides the calx of manganese, which are known, *per se*, to afford dephlogisticated air, or a mixture of this with fixed air, it was natural to conclude from analogy, that such substances upon the application of volatile alkali would not fail to afford nitrous air.

It is best, however, in these matters to trust as little as possible to conjectures, and to bring every opinion to the test of experiment. Manganese is so singular a substance, that it is perhaps hardly safe, from what happens in making trials with it, to infer in any instance of another calx of a metal a similarity of effect. Red lead, however, is known to agree in such a variety of chemical effects with manganese, that I find it difficult to persuade myself that the volatile alkali properly applied to it would not yield nitrous acid or nitrous air ; yet I have hitherto in vain attempted to bring this about. The red lead, indeed, melts during the process, flows into the cooler parts of the tube, and often obstructs the passage of the air ; but in some trials a great deal of air has been collected before that happened, and without any symptom of a nitrous mixture. It seems difficult to explain the reason of the failure ; perhaps with a better adapted apparatus, and more perseverance, either the production in question may be obtained, or the cause of the failure discovered.

17. With calcined green vitriol I had much better success. The salt was calcined to whiteness, and put into a gun-barrel; and, after several trials of forcing the volatile alkali through the hot tube, I procured by the operation some ounces of strong nitrous air.

So extraordinary an effect would no doubt have proved highly grateful to the ancient chemists, and have been by them denominated a transmutation.

In the course of my enquiries, I considered this experiment as important, because it proved, that the same combinations might take place when substances were made use of different from manganese.

18. As calcined green vitriol, *per se*, in a strong heat yields dephlogisticated air, I had now no doubt but that any substance which had this property might, by similar treatment, be made to afford nitrous air.

But in this supposition I was entirely mistaken. The volatile alkali was applied to some calcined alum at the moment when it was yielding in a strong heat plenty of dephlogisticated air. The product was an astonishing quantity of inflammable air, mixed with hepatic air and actual sulphur. The residuum of the alum had a strong hepatic smell, and contained particles of perfectly formed sulphur.

Most of these experiments, if not all, were repeated in earthen tubes instead of gun-barrels, and with the same success.

19. It now only remains, that I should briefly propose what occurs to me as the probable theory and explanation of the facts related.

The ingredients which enter into the composition of nitrous acid seem to be the two principles or elements of the atmosphere,

sphere, *viz.* phlogisticated and dephlogisticated air. That this is the case, there seems little reason to doubt. Both the composition and decomposition of nitrous acid renders the supposition probable. For,

1. Nitrous air and dephlogisticated air by mixture produce nitrous acid; and nitrous acid, by mere heat, is converted into a mixture of phlogisticated and dephlogisticated airs.

2. Nitrous air, by the methods already related, is changed into phlogisticated air, and these methods seem to consist in abstracting from the nitrous air a quantity of dephlogisticated air.

3. When nitrous acid and nitre are produced in a natural way, the process is not well understood; but the presence of the atmosphere is known to be necessary.

4. Mr. CAVENDISH's experiment is decisive on this point. The union of the two airs in question is effected by means of the electrical spark, and nitrous acid is the product.

In the next place we are to consider, that volatile alkali contains phlogisticated air; for,

1. Volatile alkali, by mere heat, or by the electrical spark, is changed into a mixture of phlogisticated and inflammable air; and,

2. The residuum of volatile alkaline air, after the calces of lead have been revived in it, is phlogisticated air.

Therefore, when volatile alkali, in the form of fume or air, is applied to red-hot manganese, or calcined green vitriol (substances which are then yielding dephlogisticated air), with these facts in view, it seems not difficult to conceive, that one of the ingredients of the alkali, *viz.* phlogisticated air, should combine with dephlogisticated air, and form nitrous acid or nitrous air. If nitrous acid be formed, it will indeed in that

heat, as has been observed, be instantly decomposed ; but if the effect of the union be nitrous air, that will sustain the heat without decomposition. How it happens, that nitrous air should be formed, and not nitrous acid, or what the reason is, that nitrous air can sustain a red heat without decomposition, when nitrous acid cannot, I am unable to say ; and it is better to acknowledge our ignorance than advance groundless conjectures. So much, I think, may be pronounced as certain, *viz.* that nitrous air contains less dephlogisticated air than nitrous acid ; because it requires the addition of dephlogisticated air to become nitrous acid.

And, lastly, if I mistake not, the experiment with the calcined alum proves, that, in order to produce nitrous air, it is not sufficient merely to apply volatile alkaline air to a substance which is actually yielding dephlogisticated air.

Perhaps the presence of another substance is required, which has a strong attraction for phlogiston. Perhaps, in the experiments with the calces of manganese and of iron, the inflammable principle of the volatile alkali combines with the calces of the metals, and the phlogisticated air, the other component part, unites with the dephlogisticated air ; and if so, it seems not improbable to suppose, that when alum is made use of, the inflammable principle of the volatile alkali having little or no attraction for clay, the basis of the alum, should combine with its acid and form sulphur. If this reasoning be true, then it follows, that the vitriolic acid has a stronger affinity to the inflammable principle than it has to phlogisticated air ; and the process with the green vitriol and manganese is to be explained by the operation of a double affinity : the inflammable principle of the volatile alkali joins with the calx of iron, the basis

basis of the vitriol, or with the manganese, and the phlogisticated air with the dephlogisticated air produced by the acid in the red heat.

Those who chuse to reject the doctrine of phlogiston must make the necessary alteration in these expressions; but the reasoning will be much the same.

